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NRL Memorandum Report 1799

**Detector Investigation for 8-15
and 100-4000 Micron Regions**

**Report No. 24-Final Report
for Period 1 July 1965 to 30 June 1967**

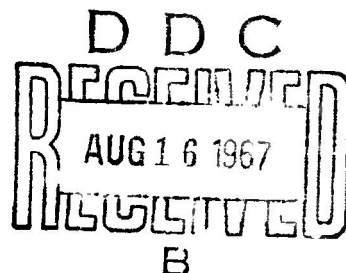
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Solid State Division

July 26, 1967



**NAVAL RESEARCH LABORATORY
Washington, D.C.**



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TABLE OF CONTENTS

	Page
Section I Introduction	1
Section II Magneto-Optical Properties of InSb	5
Section III Materials Preparation	8
Section IV Theory of SIRR Systems	12
Section V Personnel	21
Section VI Publications and Talks	22
Section VII Appendix, Liquid Encapsulation Zone Refining (LEZOR)	A-1

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Detector Investigation for 8-15 and 100-4000 Micron Regions

ARPA Order No. 269-62, Program Code No. 6 E 30

Contractor: Naval Research Laboratory, Semiconductors Branch

**Date of Contract: 12 September 1961, renewed 1 May 1963,
30 August 1965.**

Amount of Contract: \$250,000

ONR Project Order No. PO-6-0074

Contract Expiration Date: 30 June 1967

Project Scientist: H. Shenker

IDS Code 172, Ext. 2594

This research is part of Project Defender, sponsored by the Advanced Research Projects Agency, Department of Defense, via the Office of Naval Research.

Report No. 24

Detector Investigation for the 8-15 and 100-4000 Micron Regions

I. INTRODUCTION

This Report is the final report for the two year period of this contract. Since most of the work in previous reports has been published or is about to be published the present Report will cover only the work accomplished since 1 January 1967.

The following is a summary of the work accomplished during the entire period of this contract:

1. The study of impurity levels in germanium was continued. The emphasis was placed on the deep acceptor dopants in germanium since these systems have proved to be important for practical infrared detectors. The excited levels of Hg, Cd, and Be in germanium were investigated. Although some differences were found among the spectra of these dopants, the general pattern of the excited levels were quite similar to the excited levels of shallow acceptors in germanium.

2. An extensive set of studies of magneto-optic effects in InSb were carried out. It is felt that the magneto-optic absorption by shallow donors is now well understood. The study of magneto-optic absorption processes in p-type InSb have revealed some surprising results and are continuing. The recent magneto-optic work on InSb is described in Section II of this Report.

3. The mechanism of the far infrared InSb detectors has been found to be that of a free electron bolometer. The characteristics of the energy transfer mechanisms in this system has been investigated. It was shown that at the higher electron temperatures the principal mechanism involved the optical phonons.

4. The set of doped germanium detectors has been augmented by the development of the Be-doped germanium detector. This detector is sensitive to wavelengths as long as 52 microns. A Be-doped germanium detector which used a cold crystal quartz filter in front of the detector element had an effective spectral range between 40 and 52 microns and a normalized detectivity, $D^*(50\mu, 1000 \text{ cps}, 1 \text{ cps})$, of $9 \times 10^{10} \text{ cm-cps}^{\frac{1}{2}}\text{-W}^{-1}$. Another Be-doped germanium detector which contained a Be concentration of $1 \times 10^{16} \text{ atoms cm}^{-3}$ showed little or no structure associated with the lattice absorption bands of germanium. This feature makes this detector advantageous for a number of applications.

5. Methods of preparing epitaxial films of Cd_3As_2 were developed. In addition ingots of the alloy system $\text{Cd}_3\text{As}_2\text{-Zn}_3\text{As}_2$ were prepared. It was found that the conductivity type of this alloy system changed from n-type to p-type as the percentage of Zn_3As_2 increased above 50 mol percent. Preliminary preparations of Cd_3P_2 have been made in anticipation of the preparation of ingots of the $\text{Cd}_3\text{As}_2\text{-Cd}_3\text{P}_2$ alloy system. The recent aspects of this work are described in Section III of this Report.

6. Rollin detectors have been prepared which are sensitive to wavelengths as short as 80 microns by the use of Se-doped InSb. This development is of importance since fast, sensitive detectors have not previously been available for the 120 to 200 micron wavelength region.

7. Further efforts were made to improve the performance of the magnetically tuned InSb detectors. It was previously found that by using thin detector elements a high resolution detector was obtained. The present work was directed toward improving the detectivity of these detectors. While this effort has not been completed, a typical normalized detectivity, $D^*(72\mu, 780 \text{ cps}, 1 \text{ cps})$, of $2.8 \times 10^{10} \text{ cm-cps}^{\frac{1}{2}}\text{-W}^{-1}$ has been achieved.

8. A liquid encapsulation method of zone refining (LEZOR) is being developed. This method has application to the purification of semiconductor materials which have one or more components with appreciable vapor pressure at the melting point of the material. Using this method, zone-refined Cd_3As_2 was prepared. The minimum electron concentration achieved was $1 \times 10^{18} \text{ cm}^{-3}$. It is felt that this minimum is not determined by impurities in the compound but is rather an intrinsic property of the material. The work on the horizontal LEZOR method is described in Section III of this Report while a description of the vertical LEZOR method is given in the Appendix which is a copy of a paper to be published shortly.

9. A new development during this period was the study of super-heterodyne infrared radiometer (SIRR) systems. These systems have been made feasible by the development of visible and infrared lasers which can be used as local oscillators. They have the advantage over other detectors of having a very high detectivity for a very narrow spectral region. For a large part of the infrared spectrum it is shown that the detectivity limit of these detectors is set by the fluctuations of the background radiation in the very narrow spectral region for which the detector is sensitive. This work is described in Section IV of this Report.

In Section V a list of the personnel involved in this work is given. In Section VI of this Report, a list of publications and talks made in connection with this project is presented.

II. MAGNETO-OPTICAL PROPERTIES OF InSb

Work on the magneto-optical properties of InSb has continued with the investigations of conduction band combined resonance and acceptor impurity magnetoabsorption. Combined resonance entails an electric dipole transition in which both the orbital and spin vectors of an electron are changed. This transition occurs in the range of wavelength and magnetic field in which the cyclotron resonance of free and bound electrons was studied previously.⁽¹⁾ In acceptor impurity magnetoabsorption, transitions occur between the ground state or a low-lying excited state of an acceptor impurity and various light hole levels. These transitions were discovered when measurements reported earlier⁽²⁾ on InSb doped with Cd, Zn, and Ag were extended to higher fields and performed with different sample geometry and polarization of the radiation.

Both combined resonance and impurity magnetoabsorption are of considerable interest in themselves, in particular since they should occur in other materials as well as in InSb. In addition, they give detailed information concerning the band structure of InSb in a magnetic field by means of intraband transitions. This is of interest because of the recent work of Pidgeon et al.,^(3,4) in which the analysis of interband transitions in InSb yielded a detailed band structure. The analysis involved the determination of eight parameters, some of which had to be obtained from earlier intraband experiments. These parameters are not known accurately because of the difficulty of observing valence band cyclotron resonance, and of

measuring conduction band g-values over a wide magnetic field range. Furthermore, the interband experiments may be complicated by exciton effects.

A preliminary report on the combined resonance work was published recently in Physical Review Letters.⁽⁵⁾ Aside from being the first observation of the theoretically predicted transition $\hbar\omega_c = \hbar(\omega_c + \omega_g)$, this work is of value basically in two ways. First, it gives the magnetic field dependence of the four lowest conduction band energy levels over the range 50-100 kG, and thus the g-values for the first two Landau levels in this range. Second, it shows, via the observed isotropy of the combined resonance transition intensity, that non-parabolicity rather than lack of inversion symmetry is responsible for the occurrence of the transition. More recent work has focused on extending the results to lower fields, and searching for the predicted small anisotropy in the g-values. A discontinuity in the magnetic field dependence of the combined resonance transition energy has been observed in the neighborhood of 37 kG. At these fields, the energy separation of the $L = 0$ and $L = 1$ spin down Landau levels is comparable to the optical phonon energy in InSb. A polaron effect similar to that discussed by Larsen et al.^(6,7) is presently thought to be responsible for this occurrence.

Work on the impurity magnetoabsorption in p-type InSb is as yet unpublished. Studies have been made of the transmission near 10°K of samples containing about 10^{15} Cd atoms cm^{-3} . The transmission was observed in the wavelength range 15-33 microns at fields up to 111 kG. Typical spectra are shown in Fig. 1. The transmission minima shift to

lower fields were observed at lower photon energy. Figure 2 shows a "fan chart" constructed from a succession of spectra obtained at different photon energies. The straight lines drawn through the data indicate the field dependence of the energies at which individual transmission minima occur. By comparison with the work of Pidgeon et al., referred to previously, it has been concluded that the minima correspond to transitions from the acceptor impurity ground state or low-lying excited state, to the light hole Landau levels or to impurity states lying very close to the latter. The level assignments made in the figures follow the notation of Pidgeon et al. In Fig. 3 the valence band levels and impurity ground state are shown for a field of 100 kG. The impurity state is assumed to be about 13 meV below the lowest energy hole level. The light hole levels are those obtained by Pidgeon et al., while the heavy hole levels are drawn for a mass of $0.4 m_0$. Transitions to levels $a^+(2)$ through $a^+(7)$ and $b^+(1)$ through $b^+(6)$ have been observed. While many details remain to be worked out, it is felt that a basic understanding of the effect has been achieved. In particular, the relationship of the present effect to the single absorption lines observed in similar samples, as described earlier⁽²⁾, has not yet been examined.

III. MATERIALS PREPARATION

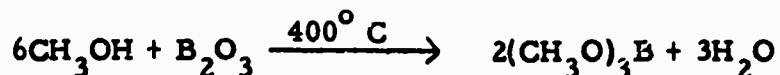
A major portion of the materials effort during this period was devoted to the development of the liquid encapsulation zone refining (LEZCR) technique. Work on vertical LEZOR was completed and a paper entitled "Liquid Encapsulation Zone Refining (LEZOR)" was accepted for publication in the September 1967 issue of the Journal of the Electrochemical Society. A copy of this paper is included as an appendix.

LEZOR is an acronym which stands for liquid encapsulation zone refining. In this technique a liquid (presently B_2O_3) is used to cover the melt and prevent the molten charge from contacting the boat. It also prevents decomposition of the molten material (i.e., GaAs, InAs and Gd_3As_2) when the vapor pressure is less than 1 atmosphere. When fully developed LEZOR could make a major contribution to the zone refining of materials which decompose at their melting point or for which no satisfactory boat material is known.

Severe fracture of the ingot caused by the freezing of B_2O_3 limits the usefulness of vertical LEZOR to material purification and exploratory investigations. If the B_2O_3 were removed while it was still liquid the technique could also be extended to single crystal growth of high purity materials in a single operation. To accomplish this end we have begun an investigation of horizontal LEZOR.

At present we are studying the removal of B_2O_3 as gaseous methyl borate at $400^\circ C$. When a 100% methyl alcohol vapor is substituted for the

inert gas atmosphere, the methyl alcohol reacts with the B_2O_3 according to the following reaction:



In the absence of any semiconductor or metal the reaction proceeds rapidly and there is only a small carbonaceous residue. When a germanium ingot was added but not melted the reaction also went to completion rapidly.

When a germanium ingot was zone leveled in a quartz boat with B_2O_3 the reaction of methyl alcohol and B_2O_3 did not go to completion but was halted by a black residue which prevented the methyl alcohol from contacting the B_2O_3 . Spectrographic analysis of the residue shows very strong lines of Si and Ge. The Si is readily explained since the B_2O_3 seriously attacked the quartz boat. Test runs on pyrolytic BN boats indicate that BN will be satisfactory but none are presently available for testing. The presence of Ge is not as readily explained. During the first 2 or 3 zone leveling passes on Ge there are numerous bubbles in the B_2O_3 which appear to react with the Ge and leave a residue when they rise to the surface. Even B_2O_3 heated to $1200^\circ C$ in vacuo overnight is known to contain .1 to .2 wgt. % water. This residual water could be reacting with the Ge to give GeO in the B_2O_3 . Plans are being made to prepare very dry B_2O_3 in order to test this idea. Since this might also be a reaction peculiar to Ge other materials such as Sb, Al and InAs will be zone leveled and the results compared.

As previously reported sound, well-characterized single crystals of Cd_3As_2 can be grown from the vapor phase on $\text{Cd}_{3-x}\text{Zn}_x\text{As}_2$ substrates. But the number of carriers has remained constant at $1-2 \times 10^{18} \text{ cm}^{-3}$. In an effort to reduce the number of carriers purification of Cd_3As_2 by vertical LEZOR was carried out. However even when 35 zone refining passes were made the minimum carrier concentration in the ingot was $1 \times 10^{18} \text{ cm}^{-3}$. This same result was found on an ingot subjected to only 6 zone refining passes. The consistency of these results indicates that the carrier concentration is not indicative of impurities but is possibly a stoichiometric phenomena. Failure to observe any substantial reduction of carriers with LEZOR casts serious doubts on the validity of the results published by the Russian workers Ugai and Zyubina.⁽⁸⁾ British, French and U. S. workers known to be working with Cd_3As_2 have also been unable to prepare Cd_3As_2 having less than $10^{18} \text{ carriers cm}^{-3}$.

Some work on the preparation of Cd_3P_2 was prepared by putting stoichiometric quantities of phosphorus and cadmium at opposite ends of a sealed quartz tube. The cadmium was held at 720°C and the phosphorus at 425°C . There was a vapor phase reaction of the two elements with Cd_3P_2 depositing near the center of the capsule. The progress of the reaction was observed and when the cadmium had all vaporized the furnaces were shut off. The resultant material was then used as source material and small crystals of Cd_3P_2 were prepared by sublimation using pure hydrogen as the carrier gas. The source was held at 525°C and the deposition region at 475°C .

Most of the deposition occurred at about 490°C . These conditions are the same conditions used to grow epitaxial Cd_3As_2 indicating that it should be relatively easy to grow mixed layers of $\text{Cd}_3\text{As}_{2-x}\text{P}_x$.

Also during this period small crystals of Cd_3As_2 were grown using AsH_3 in hydrogen and elemental Cd as source material. Presumably Cd_3P_2 could also be grown using Cd and PH_3 this would give us another and perhaps more flexible means of growing epitaxial layers of the $\text{Cd}_3\text{As}_{2-x}\text{P}_x$ alloys.

IV. THEORY OF SIRR SYSTEMS

The present theory refers to the development of high-sensitivity, narrow-band infrared detector systems using the superheterodyne infrared radiometer principle (SIRR). This type of system has been known for a long time in the microwave spectral region. With the advent of infrared lasers for use as local oscillators, it is possible to extend it to the infrared spectral region.

Referring to Fig. 4, assume that there are two beams of radiation polarized in the same direction incident on a point in space P. The net voltage V at the point P is then given by

$$V = V_{LO} \cos \omega_{LO} t + V_S \cos \omega_S t$$

where ω_{LO} and ω_S are the angular frequencies of the two beams and V_{LO} and V_S are the amplitudes of the two beams respectively. If there is a radiation detector at the point P whose output voltage E_d is proportional to the square of the radiation voltage at P and which has a time constant τ then the output voltage of the detector at time T due to the two beams is given by the equation

$$E_d = \frac{R}{\tau} \int_0^T V^2 \exp\left(\frac{t-T}{\tau}\right) dt$$

where R represents the responsivity of the detector. If both ω_{LO} and ω_S are much greater than τ^{-1} , and $|\omega_{LO} - \omega_S|$ is much less than τ^{-1} then the above expression for E_d simplifies to

$$\frac{E_d}{R} = \frac{1}{2} V_{LO}^2 + \frac{1}{2} V_S^2 + V_{LO} V_S \cos (\omega_{LO} - \omega_S) t$$

Since the power P of each beam is proportional to V^2 this equation may be written in the form

$$\frac{E_d}{R} = P_{LO} + P_S + 2\sqrt{P_{LO}P_S} \cos (\omega_{LO} - \omega_S) t$$

where the units of R are properly adjusted for the change of variables. The detector voltage is thus seen to consist of a dc portion and an oscillating portion $2\sqrt{P_{LO}P_S} \cos (\omega_{LO} - \omega_S) t$. The rms value of the last term is $(P_{LO}P_S)^{\frac{1}{2}}$. In the usual operating pattern, the local oscillator power P_{LO} is much greater than the signal power P_S so that the rms signal is much larger than the P_S term. The detector noise due to the local oscillator is proportional to the square root of the local oscillator dc signal so that the signal (rms) to local oscillator noise ratio is independent of the local oscillator power. For an ideal local oscillator and no other noise source, the noise equivalent power NEP of such a detector in a one cycle measuring bandwidth can be as low as the power equivalent of two photons per second. (9)

If the signal is incoherent wide-band radiation such as from a blackbody, then the voltage output of the detector due to the heterodyne term will have the character of a random noise-type signal. Such signals may be measured by a circuit shown in Fig. 5 in which the signal is sent through an A.C. amplifier of band width B Hz and a square law detector. The output voltage

is then measured with a suitable instrument; in order to reduce the detectivity data to the usual form it will be assumed that the band pass of this last circuit is 1 Hz.

The noise considerations of the entire system are quite different than the usual detector system. Here the signal is a noise type signal embedded with other noise signals such as those arising from fluctuations in the local oscillator power, fluctuations in the effective background radiation on the detector, and noise voltages arising in the amplifier. It turns out that it is not the magnitude of these noise signals that is important but rather the fluctuations in the output voltage caused by them.

It can be shown⁽¹⁰⁾ that the noise power per cycle $w'(0)$ in the output about zero frequency is given by

$$I_n = \sqrt{w'(0)} = \sqrt{2B(w_A^2 + w_B^2 + w_L^2)}$$

in the case that $B < (2\tau)^{-1}$ and the only important sources of noise are those mentioned in the previous paragraph. Here I_n is the noise voltage, and w_A , w_B , w_C are the noise power per cycle of the amplifier noise, the noise due to the effective background radiation, and the noise due to fluctuations in the local oscillator respectively.

The signal, I_s , is given by the expression

$$I_s = R'R^2P_L p_S B$$

where R is the responsivity of the detector, R' is the effective responsivity of the amplifier, square law detector and indicator system, and \bar{p}_s is the signal power per cycle.

The noise powers are given by the equations

$$w_A = R' 4kT_A r_n$$

where r_n is the effective noise resistance of the amplifier, and T_A is the effective temperature of r_n ,

$$w_B = R'R^2 P_L (2h\nu p_B)^{\frac{1}{2}}$$

where p_B is the power per cycle of the effective background radiation reaching the detector, and

$$w_L = R'R^2 (2h\nu P_L).$$

The value of p_B is

$$p_B = h\nu \lambda^{-2} (e^{h\nu/kT} - 1)^{-1} \Omega_B$$

where Ω_B is the effective solid angle of the incident radiation. This simplifies to

$$p_B = \lambda^{-2} kT \Omega_B$$

at long wavelengths.

Which of these noise sources is dominant depends on the values of λ , r_n , R , P_L , and Ω_B . The ratios between the various noise powers are given by the expressions:

$$\frac{w_B}{w_A} = \frac{\Omega_B}{4\lambda^2} \frac{R^2 P_L}{r_n},$$

$$\frac{w_B}{w_L} = \frac{105\Omega_B}{\lambda} \quad \text{for long wavelengths,}$$

$$= \frac{\Omega_B \exp(-h\nu/kT)}{2\lambda^2} \quad \text{for short wavelengths,}$$

and

$$\frac{w_L}{w_A} = \frac{R^2 P_L}{r_n 420\lambda}.$$

It can be seen that to reduce the influence of w_A it is necessary to have large values of R and P_L and a small r_n . The achievement of large R and P_L requires development work on detectors and lasers respectively. Large values of R may also be achieved by the use of transformers at the expense of a reduced bandwidth B . At wavelengths larger than 1000μ for many detectors w_A will be the dominant noise term.

At short wavelengths, w_L will be the dominant term. The wavelength at which w_B takes over from w_L depends only upon Ω_B . This wavelength varies from about 4μ for $\Omega_B = 1$ to 10μ for $\Omega_B = 0.01$.

At $10\ \mu$ and for $\Omega_B = 1$, it is found that the NEP (noise equivalent power) is $3.7 \times 10^{-18} B^{\frac{1}{2}}$ watts.

If the signal is caused by a small change of temperature over a solid angle Ω_S , the smallest change in temperature ΔT which is detectable at $10\ \mu$ is:

$$\Delta T = 1.5 B^{\frac{1}{2}} \Omega_S^{-1} \Omega_B^{\frac{1}{2}} \text{ } ^\circ\text{K}$$

The above analysis is for a point detector. Practical detectors have appreciable dimensions and this must be taken into account. The problem is that the local oscillator and the signal will have different phase relationships at different points of the detector if the two beams are not exactly collinear. For the near infrared using detectors of reasonable dimensions this will reduce the effective sensitivity of the detector to very small solid angles. This is illustrated in Fig. 6. If the local oscillator beam is perpendicular to the surface of the detector and the signal beam makes an angle θ with the oscillator beam then the distance h is given by $h = L \tan \theta$. There will be destructive interference effects if h is greater than $\lambda/2$ where λ is the wavelength of the local oscillator. For $L = 1\text{ cm}$ and $\lambda = 10\text{ microns}$, destructive interference effects will be obtained when θ is greater than 3×10^{-3} degrees. One excellent way of taking advantage of this effect is to focus the target of interest on the detector thus making the effective L very small and allowing appreciable angles between the signal

and the local oscillator beams before destructive interference takes place. The interesting feature here is that light from objects which are not in focus exhibits interference effects and is therefore strongly discriminated against. Another way of dealing with the situation is to use a small detector or a sharply focussed laser beam on the detector. There will also be interference effects in the thickness direction of the detector. These can be handled by using detectors having large absorption coefficients so that the effective penetration into the detector is small.

One of the problems in the SIRR system is that a broad band amplifier must be used with the system and the noise of this amplifier is a limiting factor. It was found that by using a large amount of local oscillator power, the detector element itself could be made non-linear with signal power and it could serve as its own second detector. The increased local oscillator power served both to bring the detector into a non-linear region and to raise the signal amplitude. This effect makes the instrumentation for the SIRR system identical to the instrumentation required for broad band detectors, namely an amplifier and a narrow-band voltmeter (i.e. wave analyzer or lock-in amplifier).

It can be shown that a similar effect at large local oscillator powers should occur with most semiconductor detectors. It is a matter of engineering the detector material so that the local oscillator power required is not prohibitive.

The SIRR system was tested using a Rollin detector and a 5 mm klystron as a local oscillator. At first, the self-rectification method was tried in which the detector is biased so that its responsivity is non-linear with the incident power and a signal should appear at the chopping frequency. A strong signal was observed but was found to be caused by the reflection of klystron energy back to the detector by the chopping wheel. It was found to be impossible to remove this effect so that this approach had to be abandoned. At short wavelengths where diffraction effects are greatly reduced, it should be relatively easy to eliminate this effect.

The system now being employed utilizes a wide-band amplifier with a filter eliminating the chopping frequency. Using a blackbody source at 1000°K a signal could not be detected. However a theoretical calculation showed that with the parameters of the system, the minimum detectable temperature difference was of the order of $10,000^{\circ}\text{K}$. A hotter source and a detector with higher responsivity are being substituted in order to obtain an observable signal.

A heterodyne experiment utilizing two rf generators with a Rollin detector as the mixer element was performed. The circuit used is shown in Fig. 7. The outputs of the two rf generators were passed through a single coil surrounding the detector. The detector output suitably corrected for the variation of the output of the variable frequency generator with frequency was measured as a function of the frequency difference between the two rf

generators. As shown in Fig. 8 this variation took the expected form of $(1+\omega^2\tau^2)^{-1}$. As expected the value of τ was found to decrease as the detector bias was increased. This method appears to be a very suitable method for measuring the time constant of this type of detector.

V. PERSONNEL

This Project is under the general direction of R. F. Wallis and H. Shenker. Dr. Wallis has been on leave of absence since September 1966. E. M. Swiggard was responsible for the materials preparation work; during the last year he was assisted by O. Imber. The work on the Rollin detector and the magneto-optic studies of InSb was done by Dr. R. Kaplan with the assistance of Dr. S. G. Bishop and Dr. B. D. McCombe. The work on the tuned InSb detector, the germanium detectors, and the absorption spectra of impurities in germanium was done by W. J. Moore. The optical measurements on Cd_3As_2 , Zn_3As_2 and their alloys were done by Dr. E. D. Palik and Mrs. B. W. Henvis. The other members of the Semiconductors Branch were called upon for much advice and assistance.

VI. PUBLICATIONS AND TALKS

The following publications and talks were issued during the period of this contract.

A. Publications

1. W. J. Moore, "Excited States of Neutral Zinc, Copper, and Mercury in Photoconducting Germanium," *Solid State Comm.* 3, 385 (1965).
2. E. M. Swiggard and H. Shenker, "Preparation of Doped Germanium for Far Infrared Detectors," *J. Electrochem. Soc.* 113, 92 (1966).
3. R. Kaplan, "Magneto-Optical Study of Hydrogenic Donor Impurity States in InSb," *J. Phys. Soc. Japan* 21, Suppl., 249 (1966).
4. R. Kaplan, "Magneto-optical Studies of Solids Using Fourier Transform Spectroscopy," *Appl. Opt.* 6, 685 (1967).
5. H. Shenker, E. M. Swiggard, and W. J. Moore, "Photoconductive and Electrical Properties of Uncompensated Beryllium-Doped Germanium," *Trans. of the Metallurgical Soc. of the AIME* 239, 347 (1967).
6. R. Kaplan, E. D. Palik, R. F. Wallis, S. Iwasa, E. Burstein, and Y. Sawada, "Infrared Absorption by Coupled Collective Cyclotron Excitation—LO Phonon Modes in InSb," *Phys. Rev. Letters* 18, 159 (1967).
7. B. D. McCombe, S. G. Bishop, and R. Kaplan, "Combined Resonance and Electron g-values in n-InSb," *Phys. Rev. Letters* 18, 748 (1967).
8. R. Kaplan, "Infrared Absorption by Coupled Collective Cyclotron Excitation-Longitudinal-Optic Phonon Modes in InSb," *Phys. Rev. Letters* 18, 159 (1967).
9. E. M. Swiggard, "Liquid Encapsulation Zone Refining (LEZOR)," *J. Electrochem. Soc.* (to be published).

B. Talks

1. H. Shenker, "Hot-Electron Effects in InSb at Low Temperatures," March APS Meeting, Durham, N. C., March 1966.
2. W. J. Moore and R. Kaplan, "Excited States of Neutral Beryllium Impurities in Germanium," March APS Meeting, Durham, N. C., March 1966.

3. H. Shenker, "Detectors for the Far Infrared," NRL Research Progress-1966, April 1966.
4. R. Kaplan, "Magneto-optical Study of Hydrogenic Donor Impurity States in InSb," Phys. Dept. Colloq., Rensselaer Polytechnic Inst., May 1966.
5. H. Shenker, "NRL Work on Infrared Detectors," Infrared Detector Specialty Group, IRIS, June 1966, Ft. Monmouth, N. J.
6. H. Shenker, R. Kaplan, and E. M. Swiggard, "Far Infrared InSb Detectors," 14th Nat'l. Infrared Information Symp., Ft. Monmouth, N. J., June 1966.
7. R. Kaplan and E. M. Swiggard, "Impurity States in High Purity n-type InSb," APS Meeting, Minneapolis, Minn., June 1966.
8. W. J. Moore, R. Kaplan, and E. M. Swiggard, "Optical Absorption in a Magnetic Field by Acceptor Impurities in InSb," APS Meeting, Minneapolis, Minn., June 1966.
9. R. Kaplan, E. D. Palik, R. F. Wallis, S. Iwasa, and E. Burstein, "Magneto-Optical Measurements of Coupled Modes in InSb," N. Y. APS Meeting, February 1967.
10. H. Shenker, R. Kaplan, W. J. Moore, and S. G. Bishop, "Recent Work on InSb Detectors," IRIS Infrared Specialty Group Meeting, Wright-Patterson AFB, March 1967.
11. E. Swiggard, "Preparation of Cd_3As_2 and Related Compounds," IRIS Infrared Specialty Group Meeting, Wright-Patterson AFB, March 1967.
12. H. Shenker, "The Indium Antimonide Electron Bolometer," Heat Div. Colloq., Nat'l. Bur. Stand., Washington, D. C., April 1967.
13. R. Kaplan, "Photoconductivity in InSb and Its Application to Basic Research Problems," Physics Dept., State Univ. of N. Y., April 1967.
14. E. M. Swiggard, "LEZOR (Liquid Encapsulation Zone Refining)," Electrochemical Society Meeting, Dallas, Tex., May 1967.

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1. R. Kaplan, J. Phys. Soc. Japan 21, Suppl. p. 249 (1966).
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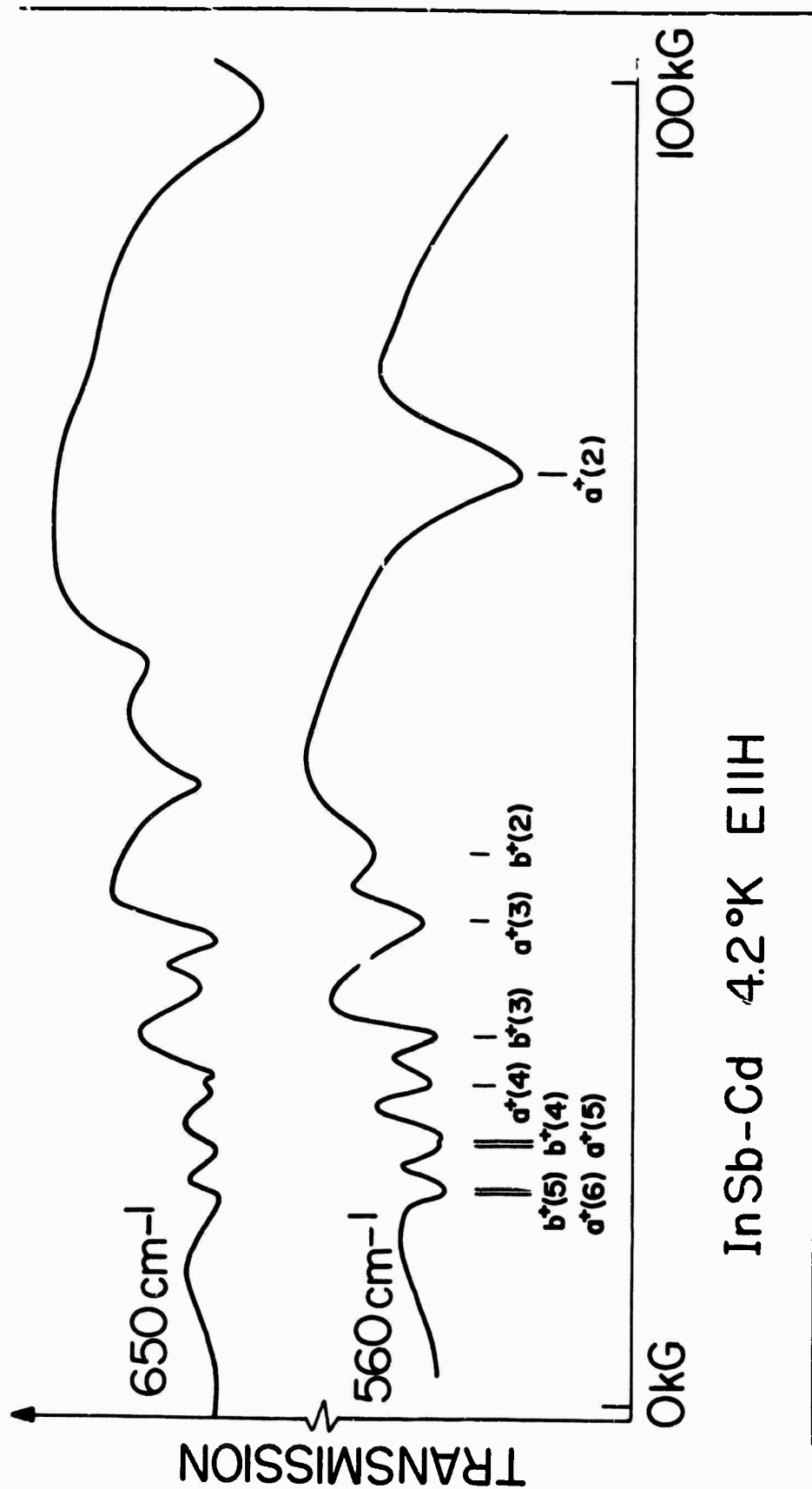


Fig. 1 - Transmission spectra obtained at two photon energies for a sample of InSb containing about 10^{15} Cd atoms cm⁻³. The transmission minima are labeled in the manner of Pidgeon et al. (3,4), to indicate the conduction band levels which serve as final states in the transitions.

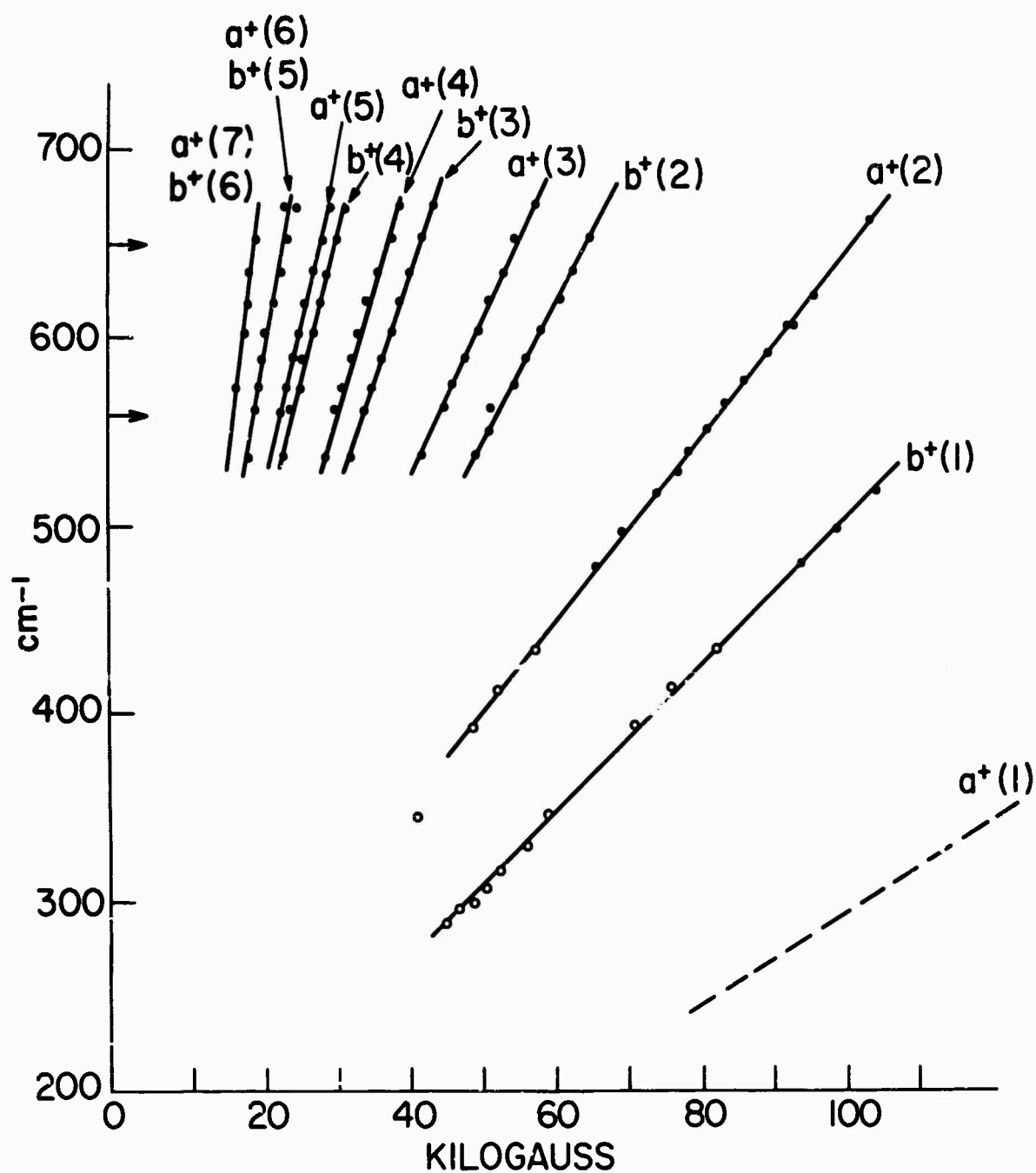


Fig. 2 - Observed dependence of spectral position on magnetic field for the impurity magnetoabsorption peaks. The arrows indicate the location of the two magnetic field scans shown in Fig. 1. The expected position of the $a^+(1)$ transition is indicated by the dashed line.

100 KILOGAUSS LIGHT HOLE ENERGIES

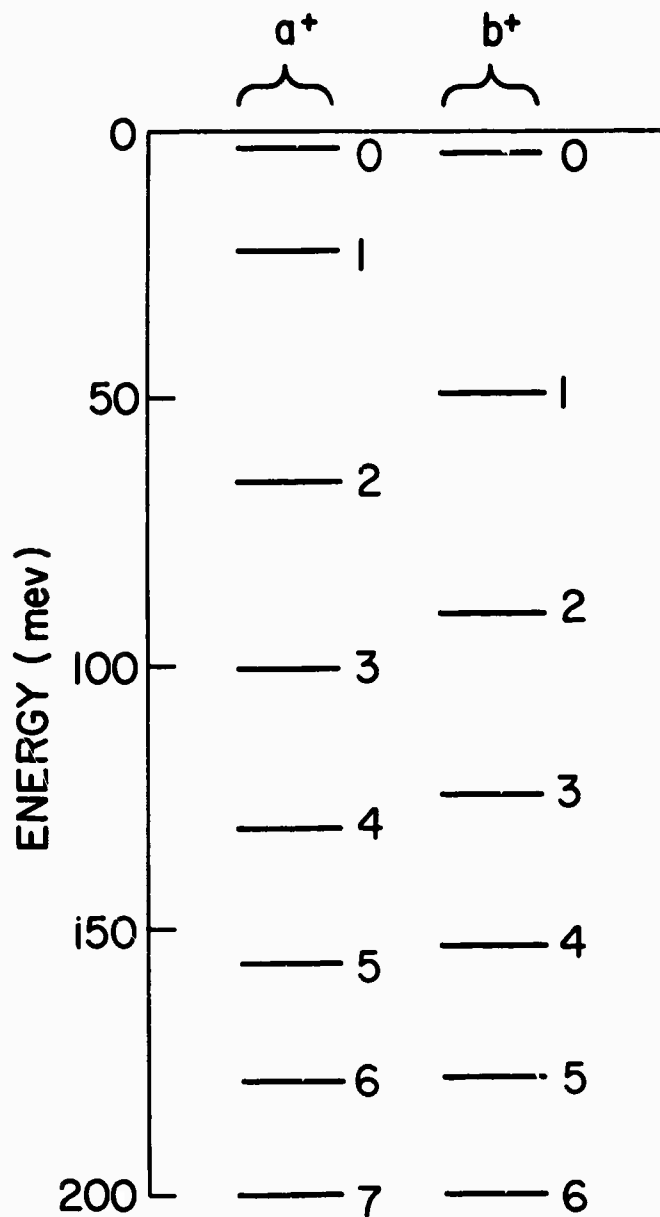


Fig. 3 - Representation of the four sets of valence band levels at $k = 0$ for InSb in a field of 100 kilogauss. The observed transitions are believed to take place between the impurity ground state, and various light hole (a^+ and b^+) levels.

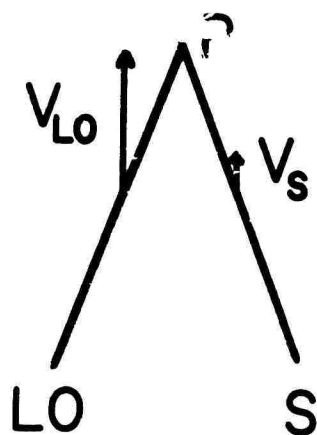


Fig. 4 - The addition of the electric vectors of local oscillator radiation and signal radiation at a point

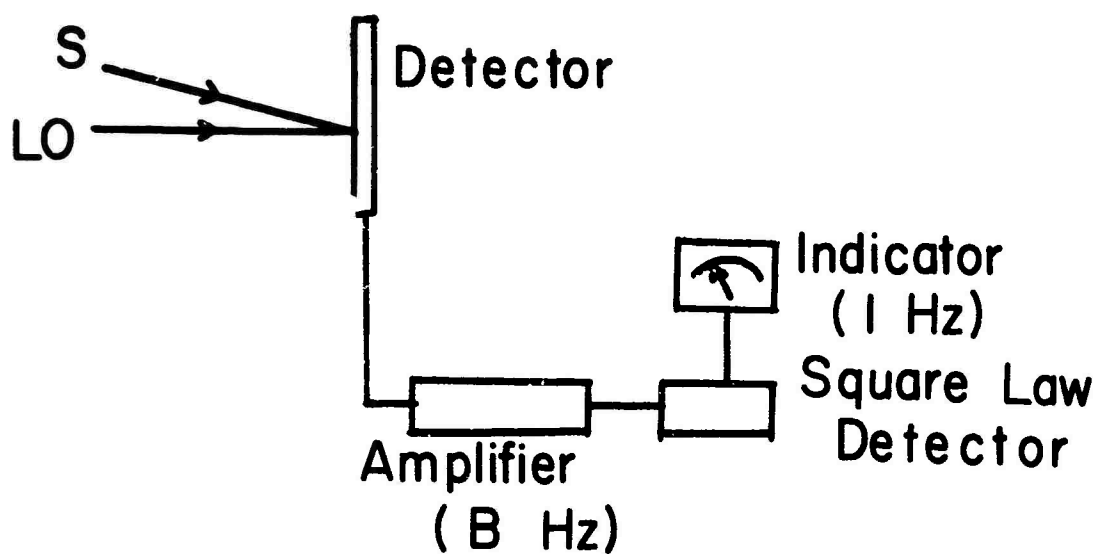


Fig. 5 - Block diagram of the measuring circuit for a SIRR detector

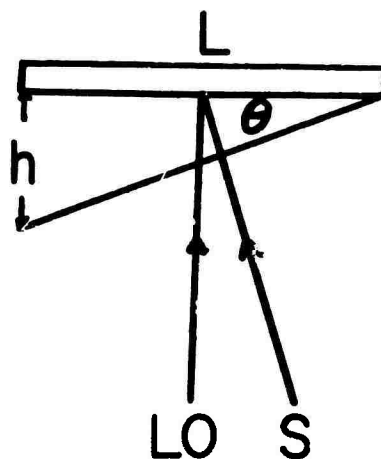


Fig. 6 - Diagram of a heterodyne detector with length L

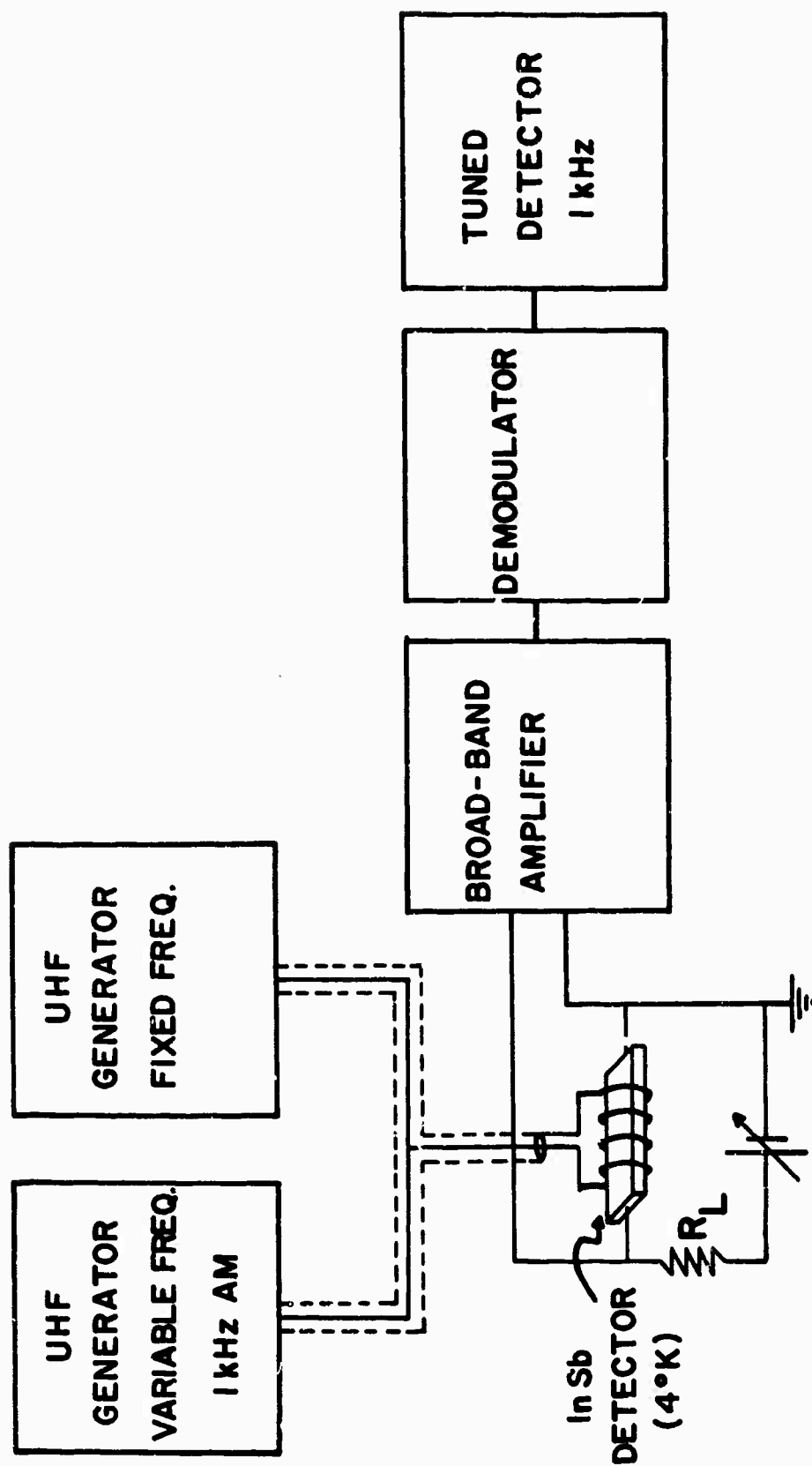


Fig. 7 - Circuit of a Rollin detector used as a heterodyne detector for two rf signals

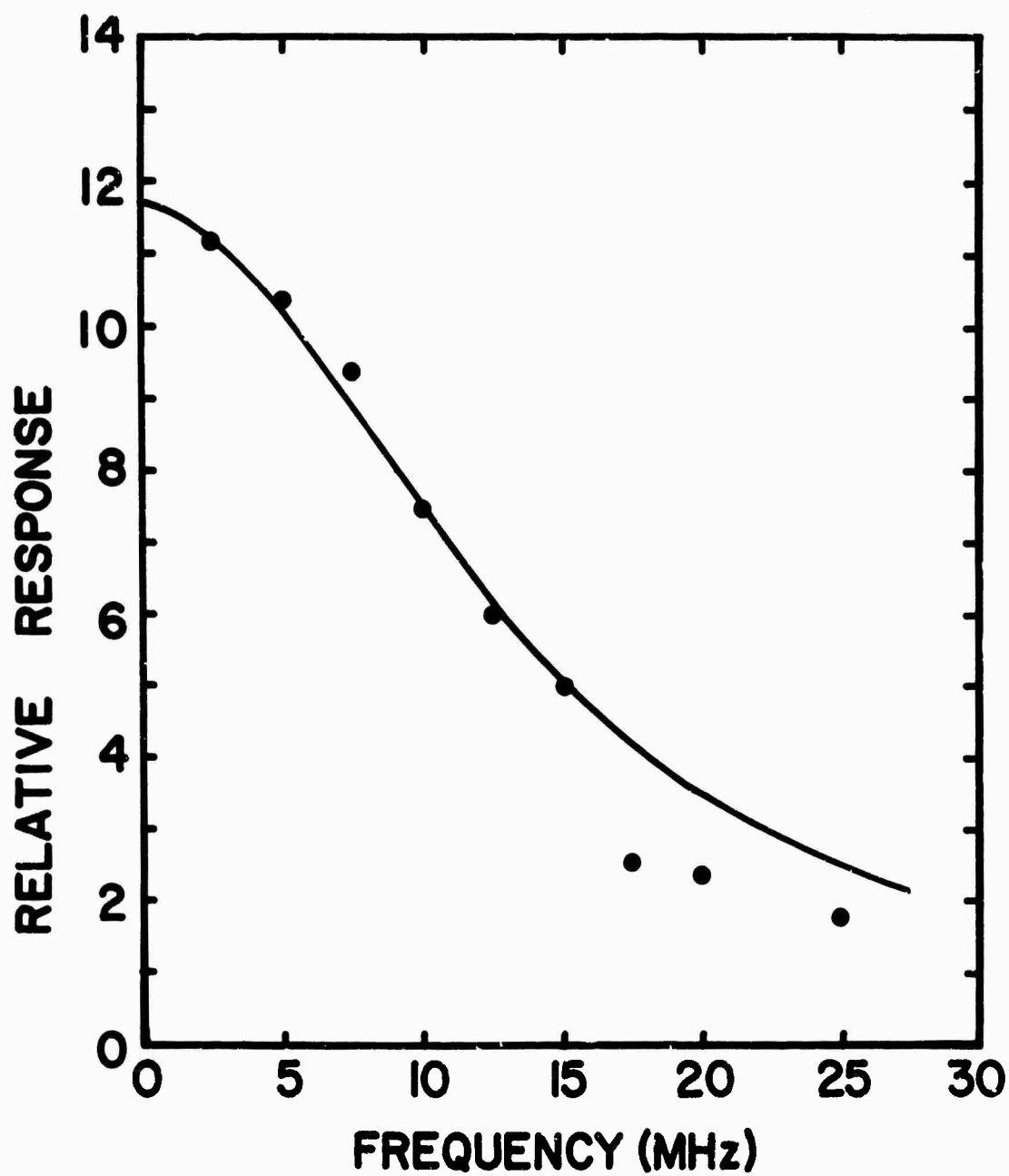


Fig. 8 - Curve of detector response vs frequency difference between two rf oscillators. Solid line is for a $(1+\omega^2\tau^2)^{-1}$ curve for $\tau=1.2\times 10^{-8}$ sec.

APPENDIX

Liquid Encapsulation Zone Refining (LEZOR)

The use of a two-liquid zone melting system was anticipated by Pfann.⁽¹⁾ He placed particular emphasis on the use of a liquid to support a large zone in a vertical ingot and to prevent contamination of the melt by a solid container. Metz, et al.⁽²⁾ and Mullin, et al.⁽³⁾ have applied the two liquid system to growth of single crystals of decomposable solids in a conventional crystal puller. They used B_2O_3 as the second liquid and found that the B_2O_3 , even though less dense than most semiconductor materials, wet the crucible and formed a liquid film between the crucible and the melt, hence the term "Liquid Encapsulation." In this work Liquid Encapsulation has been extended to zone refining. For the sake of brevity this author has adopted the acronym "LEZOR" to stand for liquid encapsulation zone refining. We report here a description of the vertical LEZOR technique and the results obtained with 40 ohm-cm Ge, InAs, Cd_3As_2 and Zn doped Ge.

A detailed schematic of the equipment used is shown in Fig. 1. The apparatus consisted of two resistance furnaces to keep the B_2O_3 liquid, an rf coil to maintain the molten zone, an open end capsule for the charge, a pedestal to support the capsule at the desired height and an outer tube to contain the atmosphere. The charge was in rod form the dimensions of which were such that it filled the capsule reasonably well but would slide readily. The capsule was heavy wall quartz (8 mm I.D. x 12 mm O.D.). One gram

of previously dried B_2O_3 was placed at the bottom of the capsule and the charge on top of this. The tip of the capsule was initially positioned in the lower furnace. The system was then evacuated and while still pumping the temperature of the furnace was raised to $650^{\circ}C$. This procedure was followed in order to remove surface moisture on the dried B_2O_3 . In the case of Cd_3As_2 (mp $720^{\circ}C$) the furnace temperature was raised to only $550^{\circ}C$. The system was kept in this condition for about 1 hour before the pump was turned off and pure H_2 admitted. After a steady gas flow was established the rf generator was turned on and the tip of the capsule moved under the rf coil. During the pump out procedure the charge slowly dropped through the molten B_2O_3 until it rested on the bottom of the capsule. An inch or more of the charge was encapsulated in B_2O_3 . The rf power was raised until a molten zone was established. The capsule was then lowered through the coil at 1 or 2 inches per hour. As the capsule was lowered the liquified charge, which was more dense than the B_2O_3 , filled the lower part of the capsule leaving only a thin layer of B_2O_3 between the capsule and the charge. During the initial pass the furnace temperature was slowly lowered to $550^{\circ}C$ and minor adjustments in rf were made. Proper shaping of the charge and careful observation during the initial pass to see that the travel did not exceed the speed with which the charge would drop through the B_2O_3 were the critical steps. If the charge was fragmented or had sharp points that could slide past the piece below it there was a strong tendency for the charge to hang

up during the initial pass. If the charge hung up the zone separated and the B_2O_3 was left behind. Melting and refreezing of a charge not encapsulated in B_2O_3 usually resulted in a broken capsule. Sometimes the separation could be corrected by pushing with the quartz rod inserted through the top of the apparatus. Due to the high viscosity of B_2O_3 the charge was sluggish in its downward movement and occasionally had to be pushed with the rod mentioned above. If the travel exceeded the speed with which the charge would fall the zone would separate and the same difficulties described above would occur. After the initial pass the zone refining process could be repeated without difficulty. The usual number of passes was 15-20 but in one case Cd_3As_2 was subjected to 35 zone refining passes. Fig. 2 is a close-up of the liquid zone in Ge. The two solid-liquid interfaces are clearly visible. Bubbles such as the ones seen in Fig. 2 were observed and they became more numerous on subsequent passes.

To complete the run the capsule was positioned so that the tip of the capsule was in the rf field but the power was lowered so that the ingot was maintained at a temperature below its melting point but above the softening point of B_2O_3 . The lower furnace was cooled to room temperature and the capsule lowered through the coil. As the tip of the capsule cooled the B_2O_3 froze and broke the capsule and ingot. In order to evaluate the run it was necessary to dissolve the B_2O_3 in water and select unbroken pieces of the ingot for electrical measurements. Various cooling cycles were tried but the ingot was always severely fractured.

A summary of zone refining results is shown in Table I. The effectiveness of LEZOR was clearly seen in the case of Ge for which it was also observed that the low field breakdown e.m.f. at 4.2°K was 2.8 V/cm. Such a low value indicates that the concentration of compensating impurities is small. Despite the fact that high purity InAs was zone refined 19 times it showed no change in carrier concentration. This probably indicates that the residual impurity has a segregation coefficient very close to one. The carrier concentration of Cd_3As_2 was reduced by a factor of 2. This result was achieved in both cases despite the fact that for the first ingot only a few passes were taken and the ratio of ingot length to zone length was only 6, while for the second ingot 35 passes were made and the ingot to zone length was 17. The factor of two reduction in carrier concentration is possibly due to improved stoichiometry and not purification.

In order to study the Liquid Encapsulation technique with respect to volatile impurities a Zn doped Ge ingot was prepared. In this case the zinc was placed in the capsule under the B_2O_3 and the usual procedure followed. Only one zone melting pass was taken. Using the published value of the segregation coefficient of Zn in Ge (4×10^{-4}) the amount of Zn required to give an ingot containing 2×10^{17} carriers/cc was added. The resulting ingot had a uniform zinc concentration of 2.5×10^{17} carriers/cc. This result clearly shows that liquid encapsulation can prevent loss of volatile impurities and can eliminate vapor phase shunting of impurities during the zone refining process. Mullin⁽⁴⁾ reports similar results pulling Zn doped Ge.

Severe fracture of the ingot presently limits the usefulness of LEZOR to material purification and exploratory investigations. It is possible that other encapsulating liquids and other capsule materials might be found to alleviate this problem. A possible solution would be to use a horizontal LEZOR process and remove the B_2O_3 by a gaseous reaction while it is still liquid. The reaction of B_2O_3 and methanol to form gaseous methylborate at $400^\circ C$ was tried and showed considerable promise.

Acknowledgments

The author is indebted to O. Imber for technical assistance in the experimental work, E. D. Palik and B. Henvis for measurement of the carrier concentration in Cd_3As_2 and H. Shenker for valuable discussions. This work was performed under Project Defender, sponsored by the Advanced Research Projects Agency, Department of Defense, via the Office of Naval Research.

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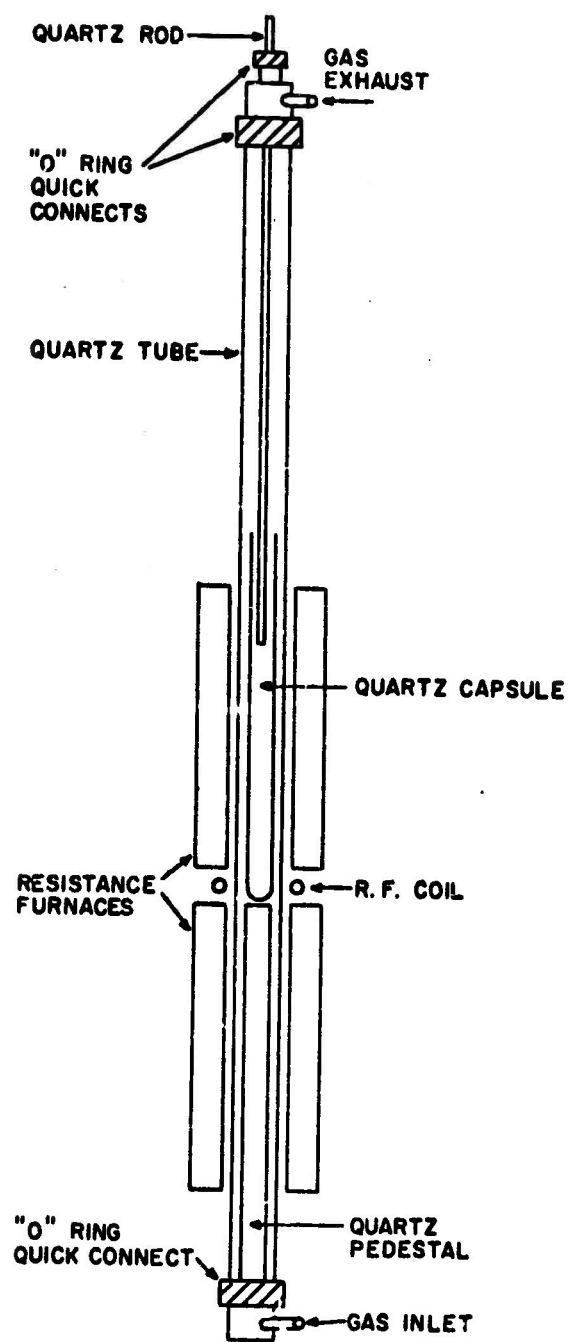
Table 1

Impurity Concentration cm^{-3}

<u>Material</u>	<u>Starting Material</u>	<u>After LEZOR</u>	<u>Zone Melting Passes</u>
Ge*	8×10^{13} (p)	2.3×10^{12} (p)	18
InAs*	2×10^{16} (n)	2×10^{16} (n)	19
Cd ₃ As ₂ **	2×10^{18} (n)	1×10^{18} (n)	6
Cd ₃ As ₂ *	2×10^{18} (n)	1×10^{18} (n)	35

* Ingot Length 23 cm - Zone Length 1.3 cm.

** Ingot Length 11.5 cm - Zone Length 1.8 cm.



LIQUID ENCAPSULATION ZONE REFINING
APPARATUS

Fig. A1 - Schematic of
LEZOR apparatus

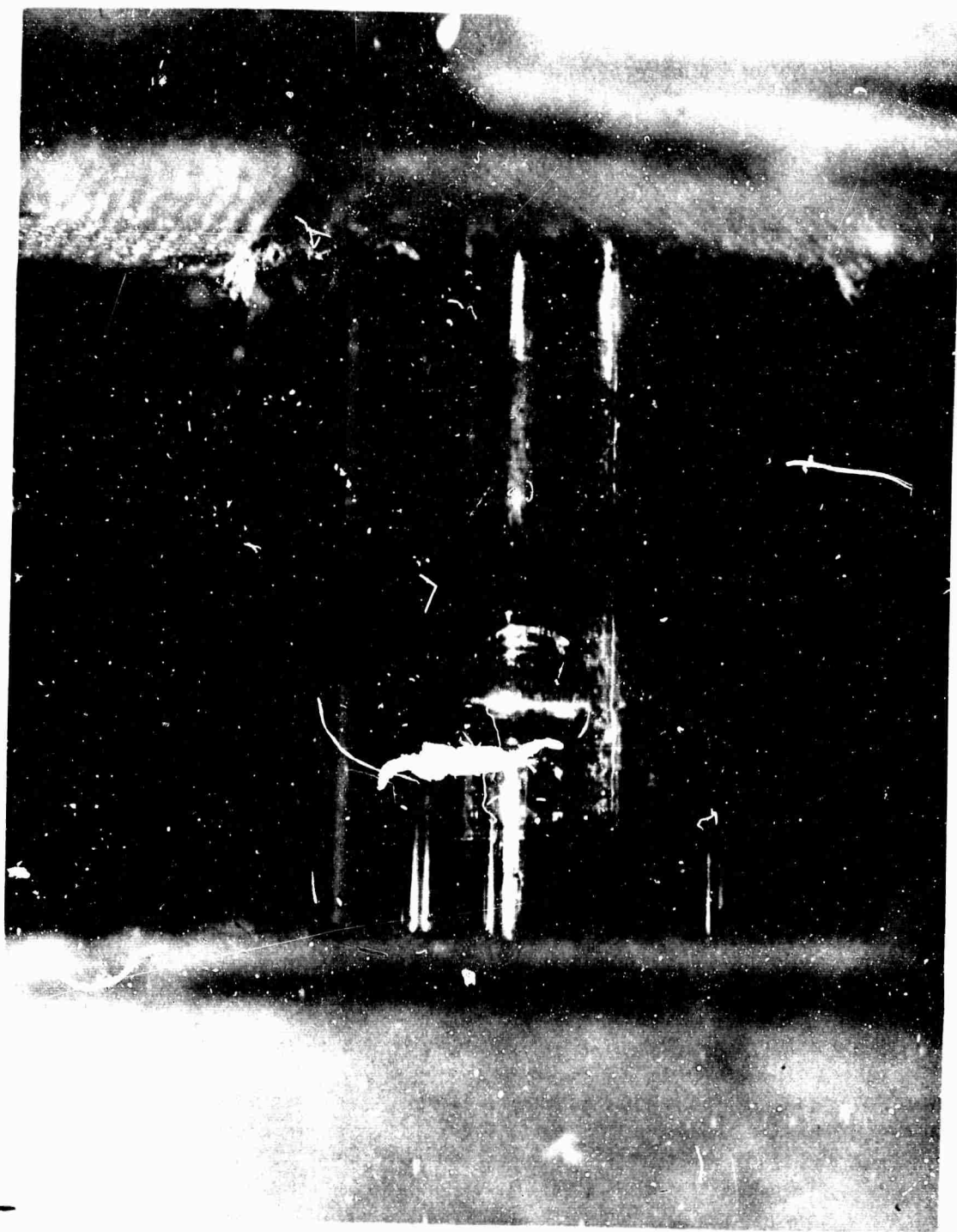


Fig. A2 - Molten zone in B_2O_3 encapsulated Ge ingot

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)		2a. REPORT SECURITY CLASSIFICATION	
Naval Research Laboratory Washington, D. C. 20390		Unclassified	
		2b. GROUP	
3. REPORT TITLE			
DETECTOR INVESTIGATION FOR 8-15 AND 100-4000 MICRON REGIONS Report No. 24 - Final Report for Period 1 July 1965 to 30 June 1967			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates)			
Final report for period July 1, 1965 to June 30, 1967			
6. AUTHOR(S) (First name, middle initial, last name)			
H. Shenker			
6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS	
July 26, 1967	44	14	
8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)		
ONR Project Order PO-6-0074	NRL Memorandum Report 1799		
b. PROJECT NO	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)		
ARPA Order 269-62, Program Code			
c. 6 E 30			
d.			
10. DISTRIBUTION STATEMENT			
This document has been approved for public release and sale; its distribution is unlimited			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY	
		Advanced Research Projects Agency, Washington, D. C. 20350	
13. ABSTRACT			
<p>This report is the final report for the two year period of the contract. Since most of the work in previous reports has been published or is about to be published, the present report will cover only the work accomplished since January 1, 1967. During the entire period of the contract: (a) the study of impurity levels in germanium was continued, (b) magneto-optic effects in InSb were extensively studied, (c) far infrared InSb detectors were investigated, (d) a Be-doped germanium detector was developed, (e) methods of preparing epitaxial films of Cd₃As₂ were developed, and ingots of Cd₃As₂ - Zn₃As₂ were prepared, (f) Rollin detectors sensitive to wavelengths as short as 80 microns by the use of Se-doped InSb have been prepared, (g) efforts toward improving magnetically tuned InSb detectors were made, (h) work on a liquid encapsulating method of zone refining was performed, and (i) superheterodyne infrared radiometer systems were studied.</p>			

14.

KEY WORDS

Infrared detectors

InSb

 Cd_3As_2

Magneto-optics

Semiconductors

LINK A

LINK B

LINK C

ROLE

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ROLE

WT

ROLE

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